Non-ecofriendly textile chemicals and their probable substitutes—An overview

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Textile auxiliaries/chemicals/speciality chemicals are scanned for their ecofriendliness or otherwise. Polyester dyeing carriers are taken as an example to illustrate this point. Observations of a German working group on this aspect of carriers are quoted. Important non-ecofriendly chemicals are cited based on the requirements of Eco-Tex Consortium of Europe. Probable substitutes for the existing non-ecofriendly chemicals are suggested. A method to examine the claims of textile auxiliary manufacturers about ecofriendliness of their products is suggested for the benefit of users. A German example of combating the ecological problem is given for the possible implementation by Indian manufacturers.

Keywords: Carcinogenicity, Dyeing carriers, Ecology, Sensitizers, Textile auxiliaries

1 Ecofriendly Textiles

Ecology is the study of interactions between living organisms and their environment, which includes atmosphere, water and pollutants. The pollutants in water and atmosphere are either present naturally, like micro-organisms, or introduced by man through industrial gases and effluents. These pollutants interfere with the natural growth of the living beings, including plants, animals and human beings. Thus, insecticides, pesticides, herbicides, chemical wastes, gases of nitrogen oxides and sulphur oxides, formaldehyde, chlorine, oil spills and radio-active contaminants have a direct bearing on the ecology of a given area.

With respect to ecology and textiles, The following three aspects should be considered:

- Production ecology, comprising (i) cultivation and harvesting of natural fibres, (ii) manufacture of man-made fibres, (iii) manufacture of threads and fabrics, (iv) bleaching, dyeing, printing and finishing of textiles, and (v) garments manufacture, with the application of fertilizers, growth regulators, crop-protection agents (pesticides, etc), dyes, pigments and textile chemicals, auxiliaries and finishing agents.

- User ecology, referring to the effects of clothing textiles and the substances that give them their beauty and performance characteristics on human beings during use, i.e. when the clothing is worn.

- Disposal ecology, referring to the disposal of the textiles after use, i.e. recycling, composting, dumping or incinerating in a manner that ensures the least possible environmental impact.

The main raw materials used in the textile industry are the textile fibres, which are spun into yarns, which, in turn, are woven into fabrics. They are further processed to get bleached, dyed/printed or finished before introduced into the consumer market. During the course of conversion of fibres into the finished fabrics, various chemicals are used for different purposes. These are known as textile auxiliaries, textile chemicals, textile process chemicals, and more recently, speciality chemicals. All these chemicals may be broadly classified into two groups: (i) the chemicals used to serve some purpose(s). After these purposes are served, the chemicals are removed from the textile material being processed and are let in the drain, causing effluent problem, and (ii) the chemicals which continue to form a part of the textile material being processed by way of either chemical reaction with the textile substrate or mechanical deposition of water-soluble or insoluble substances in the textile substrate. These chemicals are expected to remain more or less permanently, withstanding the subsequent rigorous action (of varying degrees) exerted on the end-products during their use by the consumers. These two classes may be called temporary and permanent/semi-permanent textile chemicals respectively. The temporary textile chemicals are those which are helpers/assistants and are added to
the usual processing solutions (scouring, bleaching, dyeing, after treating, finishing, etc.) for improving the efficiency of the process and/or the effect obtained on the textile materials being processed. Thus, under the category of temporary textile auxiliaries is included a variety of products having diverse properties, detergents (based on alkylbenzene sulphonate, alkyphenol ethoxylates, fatty alcohol sulphates, etc.) used in the scouring of cotton fabrics, and wetting agents (creosyl and non-creosyl) used in the mercerizing liquors, especially in the mercerization of grey cotton fabrics to help caustic soda to come into intimate contact with the cotton fibres or on the warp yarn (scouring) or swelling and subsequent mercerization of the fabric (mercerizing). After these processes are carried out, the detergent and the wetting agent are removed from the fabrics along with caustic soda and the impurities removed from the fabrics.

Levelling agents (alkylbenzene sulphonates and alcohol sulphates) used in dyeing of acid dyes on wool/nylon or in vat dyeing of cotton fabrics, carriers (dichloro- and trichloro- benzenes) and dispersing agents (naphthalene sulphonate formaldehyde condensates) used in the dyeing of disperse dyes on polyester fabrics, and solution aids (benzyl sulphanilates) used in dissolving sparingly soluble dyes in the printing pastes are some of the examples of temporary textile auxiliaries. Their presence in the processing media (dye solutions or printing pastes) is absolutely necessary from the point of view of obtaining level shades, good depth and optimum colour value in dyeing and printing. Incidentally, most of all these auxiliaries find the way in the effluents from the dyehouse. Some of the residual auxiliaries do remain on the fabrics and reach the consumers.

Stabilizers for hydrogen peroxide (sodium silicate, organophosphorous compounds and nitrogenous chelating agents) used in bleaching and the formaldehyde-based cationic dye-fixing agents used in direct and reactive dyeing also find their way into the textile effluents.

Textile chemicals belonging to the permanent/semi-permanent class are usually found in finishing processes. Softeners (anionic, cationic, non-ionic and reactive), water repellents, crease-resisting and crosslinking agents (mostly formaldehyde based), flame retardants (bromine and phosphorus compounds), rot-proofing agents, antistatic agents (mineral oil and other products), and binders and fixers (formaldehyde containing polymers) used in pigment printing are some of the examples falling in this group.

Apart from these two groups of compounds, certain other organic and inorganic compounds are also used in textile processing. Thus, inorganic and organic acids like sulphuric, hydrochloric, formic, acetic, tartaric, oxalic, citric and tannic acids; alkaliies like sodium hydroxide, sodium carbonate, potassium carbonate and ammonium hydroxide; salts like sodium chloride, sodium sulphate (Glauber's salt), diammonium phosphate, magnesium chloride, zinc nitrate, zinc chloride, zinc fluoroborate; oxidizing agents like sodium hypochlorite, bleaching powder, hydrogen peroxide, sodium chlorite, nitrous acid, potassium chlorate; and reducing agents like sodium hyposulphite, sodium thiosulphate (hypo), sodium or zinc sulphonylate formaldehyde, sodium sulphite, stannous chloride, stannous acetate, glucose and dextrin are used in textile processing. Sequestering agents like EDTA, NTA, DTPA, sodium hexametaphosphate, etc. are used to soften the hard water.

The production ecology referred to above should be as environmentally sound as possible with regard to its impact on air, water and soil as well as on human working conditions (MAK values, noise and dust control).

2 Carriers in Polyester Dyeing

Diphenyl (biphenyl), o-phenyl phenol, p-phenyl phenol, o-dichlorobenzene, trichlorobenzene, methyl naphthalene, butyl benzoate, methyl phthalimide, etc. are the most commonly used commercial carriers in polyester dyeing. Many of them have been withdrawn (not necessarily in India) by manufacturers from the market because of their carcinogenic, sensitizing or other toxic potentialities.

Commercial carriers described in technical literature are as follows:

- Butyl benzoate in lique from, organic ester, anionic aromatic ester, aromatic ester, modified

* Work place concentration in the air
aromatic ester, emulsifiable biphenyl derivative, chlorinated benzene, emulsifiable chlorinated solvent, chlorinated aromatic compound, chlorinated solvents, trichlorobenzene preparation, mixture of chlorobenzene derivatives, non-volatile phenolic derivatives, aromatic hydroxy derivative, oxydiphenyl (hydroxy diphenyl, i.e. phenyl phenols), phenolic compounds, methyl salicylate, butyl benzoate-biphenyl, modified biphenyl, methyl naphthalene, etc.

The most common ones are dichlorobenzene and/or trichlorobenzene, phenyl phenols and biphenyl, all of which are toxic/carcinogenic/sensitizing in nature and hence are not ecofriendly textile chemicals.

3 Carriers and Their Health Hazards

The Federal Institute for Health Protection of Consumers and Veterinary Medicine (BgVV), Berlin, Germany, established Textiles Working Group, which since 1992 has dealt specially with the protection of consumer health with respect to clothing textiles. This Working Group was established for the purpose of formulating general statements on the potential hazards inherent in groups of materials used in textile consumer goods, such as finishing agents, auxiliaries and colouring agents. In order to take stock of the situation, priorities shall be set for consumer health protection and research requirements are to be defined. Examples of problematic compounds and typical representatives of certain classes of substances are to be assessed for their impact on health, and recommendations on how to avoid or reduce health risks are to be worked out. Among the key issues to be dealt with are dye carriers.

Representatives of the German textile industry informed the Working Group that the finishing and dyeing of chemical fibres involve some 600 different finishing and auxiliary agents. From the toxicological point of view, the trichlorobenzene proved to be a particular problem. In the opinion of the Working Group, this substance should no longer be used as a carrier. This group also arrived at the conclusion that the use of o-phenyl phenol as a carrier is no longer in accordance with state-of-the-art technology. The Working Group was also informed that in Germany the following substances are no longer used as carriers: benzyl alcohol, biphenyl, dicyandiamide, naphthalene, perchlorethylene and 1,3,5-trimethylbenzene. It is not known to the Working Group which carriers are used abroad.

In the preliminary attempt to assess the potential health risks caused by some carriers, a number of basic problems become apparent. These include:
- The toxicological data, necessary to assess potential health hazards, are not available for some of the substances under discussion.
- Practically, no experimental data exist on the release of carriers from textiles during wearing.
- According to experts, in textiles manufactured at the current state-of-the-art technology, the carrier content is 0.2%. Basically, this exposure is low when such textiles are worn. However, if the fabrics are faultily dyed and finished, exposure is greater and a health hazard resulting from substances with a toxic potential cannot be excluded. This applies to the large amount of imported textiles.

4 A Questionnaire

The ecofriendliness or otherwise of a textile chemical can be inferred from a questionnaire issued by Eco-Tex Consortium, established by the companies Scotdic, Textil Farben GmbH, Coigne and TDG. The Textile Design Group (TDG), Milan, which is a consultancy and service enterprise, offers its services at all stages of textile manufacturing with the aim of developing ecologically optimized textiles.

This questionnaire is to be filled for each textile auxiliary/chemical by its manufacturer. The following information is solicited of the manufacturer and of the product.

Company address, product name, chemical character and certain specific information in the following format:

Does the product contain organic solvents? Yes/No
Does the product contain more than 1% halogenated solvents? Yes/No
Does the product contain more than 1% APEOs (Alkyl phenol ethoxylates)? Yes/No
Does the product contain silicone? Yes/No
Does the product contain DTDMAC (bis- (tallow alkyl)dimethylammonium chloride)? Yes/No
Does the product contain DSDMAC (Distearyl dimethylammonium chloride)? Yes/No
Does the product contain DHTDMAC [Di-(hardened tallow)dimethylammonium chloride]? Yes/No
Is the content of LAS C10-C13 Yes/No
average chain length >12 in the product
more than 1 %?
Does the product contain ABS
(Akylbenzene sulphonate)?
Does the product contain more than 1 % formaldehyde?

Textile mills/process houses should ask for this information from the textile auxiliary/chemical manufacturers and if the answer (s) to one or more questions is 'Yes', the auxiliary/chemical should not be used in the processing of textiles, implying that the products containing the following ingredients are not ecofriendly:

Organic solvents such as benzene, toluene, xylene, etc.; halogenated solvents like perchloroethylene, trichloroethane, trichloroethylene, carbon tetrachloride, etc.; octyl or nonyl phenol ethylene oxide condensate (alkyl phenol polyethoxylates); silicones including amino silicone, since in the latter, the major portion of the macro-molecule is poly (dimethylsiloxane) segment; di(tallow alkyl)dimethylammonium chloride; distearyl dimethylammonium chloride; di (hydrogenated tallow alkyl)dimethylammonium chloride; dodecyl (average C_{10}-C_{13}) alkyl benzene sulphonate; alkyl (dodecyl)benzene sulphonate; and formaldehyde (in resin pre-condensates and crosslinking agents based on formaldehyde, formaldehyde - based cationic dye-fixing agents, etc).

A broad outline of the existing non-ecofriendly chemicals used in textile processing with probable alternatives and their performance with respect to the currently used chemicals is given in Table 1.

The claims of textile auxiliary manufactures about their products regarding eco-friendliness should be considered with caution. For example, it is known that dichlorobenzene, trichlorobenzene and their mixture are very effective carriers in dyeing disperse dyes on polyester fibre materials at boil and atmospheric pressure. It is also known that these

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Non-ecofriendly chemical</th>
<th>Use</th>
<th>Alternative chemical(s)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>Pentachlorophenol</td>
<td>Size preservatives</td>
<td>Sodium silico-fluoride</td>
<td>Less effective</td>
</tr>
<tr>
<td>1 b</td>
<td>Formaldehyde</td>
<td>Size preservatives</td>
<td>Fatty alcohol ethylene oxide adduct</td>
<td>More costly</td>
</tr>
<tr>
<td>2</td>
<td>Nonyl phenyl ethylene oxide adducts (APEO)</td>
<td>Detergent, emulsifier</td>
<td>Ammonium/cationic softeners</td>
<td>Not permanent</td>
</tr>
<tr>
<td>3</td>
<td>Silicones and minosilicone+APEO emulsifier</td>
<td>Softening, water repelling</td>
<td>Hydrogen peroxide</td>
<td>More costly</td>
</tr>
<tr>
<td>4 a</td>
<td>Bleaching powder</td>
<td>Cotton bleaching</td>
<td>Nitrogenous stabilizer</td>
<td>Less efficient than sodium silicate</td>
</tr>
<tr>
<td>4 b</td>
<td>Sodium hypochlorite</td>
<td>Cotton bleaching</td>
<td>Butyl benzoate</td>
<td>Suitable, less efficient</td>
</tr>
<tr>
<td>5 a</td>
<td>Sodium silicate</td>
<td>Hydrogen peroxide stabilizers</td>
<td>Water-based thickener</td>
<td>Dull prints and harsh handle</td>
</tr>
<tr>
<td>5 b</td>
<td>Phosphorous-based compound</td>
<td>Hydrogen peroxide stabilizers</td>
<td>Water-based thickener</td>
<td>Dull prints and harsh handle</td>
</tr>
<tr>
<td>6 a</td>
<td>Dichlorobenzene</td>
<td>Carriers in polyester dyeing</td>
<td>Polycarboxylic acid</td>
<td>Less effective, costly</td>
</tr>
<tr>
<td>6 b</td>
<td>Trichlorobenzene</td>
<td>Pigment printing</td>
<td>Non-formaldehyde crosslinking agents</td>
<td>Yellowing, changing the tone of dyed fabrics, more strength loss of fabrics</td>
</tr>
<tr>
<td>7</td>
<td>Kerosene (as emulsion thickener)</td>
<td>(a) Crease resisting of cotton and its blend fabrics</td>
<td>Polyacrylic acid</td>
<td>Less effective, costly</td>
</tr>
<tr>
<td>8</td>
<td>Formaldehyde</td>
<td>(b) Dye fixing for direct and reactive dyeings/prints</td>
<td>Non-formaldehyde based products</td>
<td>Perhaps tone difference and perhaps less effective</td>
</tr>
<tr>
<td>9</td>
<td>Sodium dichromate</td>
<td>Vat dyeing</td>
<td>Hydrogen peroxide</td>
<td>Less effective in some cases, generally work well</td>
</tr>
</tbody>
</table>
carriers are human carcinogens and hence are not ecofriendly. If a manufacturer develops and markets, for example, dibromobenzene as a non-chlorobenzene, ecofriendly carrier without disclosing the chemical identity, it does not necessarily mean that the newly developed carrier is ecofriendly. If the manufacturer collects or generates the toxicity data, such as LD50 value, mutagenic and/or carcinogenic potential, skin irritation/respiratory/ sensitization potential, etc. of dibromobenzene and finds that it is free from all these toxic activities, then he can confidently describe his new product as ecofriendly, even though he does not disclose the chemical structure of the newly developed carrier.

Acetic acid, a non-ecofriendly chemical, finds many uses in textile processing, such as polyester dyeing, vat acid dyeing, etc. If it is replaced by formic acid, without declaring its structure, under fancy name, claiming that it is not based on acetic acid, it need not necessarily be an ecofriendly product.

Formaldehyde is a known respiratory sensitizer and a skin irritant and is widely used in a large number of textile auxiliaries and specialty products, such as cationic dye fixing agents (dicyandiamide-formaldehyde condensation product); DMU, DMEU and DMDHEU (all containing N-methylol groups formed by reacting formaldehyde with urea, ethylene urea and dihydroxy ethylene urea respectively); reactive softener based on methylol stearamide (using formaldehyde); and dispersing agent based on the condensation product of 2-naphthalene sulphonyl acid and formaldehyde used in vat acid process and in polyester dyeing. Formaldehyde itself is used as a crosslinking agent for cotton fabric to make it crease-resistant.

Some non-formaldehyde crease-resisting agents are in the Indian market for quite some time now obviously without disclosing their chemical structures. We have no complaint against such manufacturers for not disclosing the structures. What we object to is their claim that they are ecofriendly.

As described above, a non-formaldehyde product need not necessarily be ecofriendly. For example, if formaldehyde is replaced by another aldehyde with one or more aldehyde groups, it is technically and legally a non-formaldehyde product. Unless the other aldehyde is found out to be free from all toxic properties, it cannot be described as ecofriendly product. The user is unaware of this aspect. He assumes that any crosslinking agent not based on formaldehyde is an ecofriendly specialty product. In this case, the manufacturer may exploit the users' ignorance. We still do not maintain that the other aldehyde products are not ecofriendly; all we want to say is that the manufacturers should find out that these products do not have any toxic effects and then claim these products ecofriendly and not before.

5 A Fine Example

The goal of the German chemical industry has been the replacement of toxicologically and ecologically harmful textile auxiliaries and dyes by less problematic products and for which the following voluntary steps have been taken:

- They have voluntarily stopped using alkylphenol ethylene oxide adducts (APEOs) in textile auxiliaries, which are subject to the regulations on detergents and cleaning agents.
- They have voluntarily stopped using azo dyes based on carcinogenic amines.
- They have voluntarily stopped using low-boiling chlorinated hydrocarbons in preparations.
- They have developed reactive dyes with a higher degree of fixation.
- They have developed low-emission spin-finishing agents, softeners and winding oils.
- They have developed low-phosphorus and phosphorus-free stabilizers for peroxide bleaching.

References